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Description

The present invention relates to aqueous dispersions of fluorinated polyurethanes and to their use for textile coatings.

5 More particularly, the present invention relates to aqueous dispersions of fluorinated polyurethanes, and to their use in the preparation of textile products endowed with both high impermeability to liquid water and high breathability to water vapour.

It is well known that the textile industry has made efforts for some time to provide textile products endowed with contemporaneously high impermeability and breathability for uses in the sporting field or in
10 working clothes, or, more generally, in clothes for open-air uses, as reported in the Journal of Coated Fabrics, 1985, 15 (7), 40-66, and in Melliand Textilberichte, 1986, 67 (4), 277-287 and 67 (11), 824-829. For that purpose, as these references mention, different methods are used which can be divided into six main techniques.

A first technique consist in impregnating textile substrates with water-repellent products, such as waxes, 15 silicones, fluorinated hydrocarbons, aluminum- and chromium-salts, and so forth. In this way articles are obtained which are endowed with a good breathing level, but which show a low impermeability and a poor water-repellency upon washing and wear.

A second technique comprises the coating of thick (generally thicker than 60 g/m²) and compact layers of polyvinyl chloride, chlorinated rubbers, polyurethanes (PU), and so forth, on textiles.

20 The so-obtained articles show a high impermeability, but nearly no breathing characteristics.

The reduction in thickness of the deposited layer, sometimes down to values of approximately 30 g/m², makes it possible to obtain adequate values of breathing characteristics but severely impairs the impermeability.

As another alternative, microperforations are provided on heavily-coated materials, e.g., by means of 25 electrical discharges between high-voltage electrodes, with a minor decrease in impermeability but still with insufficient breathing characteristics.

According to a third technique, textile fabrics are coupled with films that are impermeable but endowed with breathing characteristics, such as those of polytetrafluoroethylene (PTFE) or polyester (PES).

In case of PTFE, membranes or films previously subjected to a controlled draught, so as to provide 30 pores of a diameter of approximately 0.2 μ m, are used. Such membranes are permeable to water vapor but not to liquid water.

In case of PES, the breathing characteristics are secured by the formation of labile hydrogen bonds between the molecules of the water vapor and the ester functions of the fibers of the membranes from which occurs the transportation of water vapor between adjacent ester groups.

35 These articles are very satisfactory as regards the applicative performance, but they involve the use of expensive materials and/or of a coupling technique, less diffused and more complex than a spreading or coating technique.

A fourth technique consists in using fabrics constituted by microfibers (having a count lower than 0.2 dtex), which are inherently hydrophobic in the absence of any treatments.

40 The corresponding articles have good breathing characteristics, but show considerable decrease in impermeability due to washings, abrasions, and soiling with oil, or other materials, and consequently suffer serious use limitations in the field of working clothes.

A fifth technique relates to particular coatings of two different types. One type uses polyethoxylated polyurethanes (PU's) suitable for providing the water vapor transportation by means of repeated and 45 consecutive adsorption and desorption, according to the mechanism based on the presence of labile hydrogen bonds, as above mentioned.

The other type uses solutions in volatile solvents of resins or monomers polymerizable by irradiation (Chemical Week 1986, 138 (25) 22-23) and other materials suitable to develop gaseous products, e.g., isocyanic prepolymers, which develop CO₂ in the presence of moisture.

50 But the thus-obtained textile articles generally require further treatments, such as the application of silicones, or other surface-finishing treatments.

A sixth technique provides coatings of the sponge type such as by means of the coagulation of aqueous baths of PU's dissolved in dimethylformamide, previously coated on a support fabric. This requires relatively complex facilities and expensive treatments of the effluent streams. Furthermore, to achieve 55 suitable levels of water-repellency, specific auxiliary agents are necessary, e.g., perfluorocompounds, to be introduced into the coating formulation, or applied subsequently.

It has now, surprisingly, been discovered that stable aqueous dispersions of fluorinated polyurethanes, to be mainly used for preparing textile articles endowed simultaneously with high impermeability and good

breathability, are those obtained by starting from an organic diisocyanate and a mixture comprising diols containing ionizable groups and macroglycols based on polyols and hydroxy- and/or carboxy-capped fluoropolyethers.

The principal object of the present invention is hence the provision of stable aqueous dispersions of fluorinated polyurethanes containing in their macromolecule hydrophilic ionic groups, both of anionic and cationic character, which may be obtained according to the following steps:

- (a) preparation of a fluorinated polyisocyanate, by reaction between an organic diisocyanate and a mixture comprising diols containing ionizable groups and macroglycols comprising polyols and at least 1% by weight of one or more hydroxy- and/or carboxy-capped fluoropolyethers;
- (b) salification of the thus-obtained fluorinated polyisocyanate, to convert the ionizable groups into hydrophilic cations or anions; and
- (c) dispersion and chain extension of the salified fluorinated polyisocyanate in water.

According to the present invention, the fluorinated polyisocyanate is obtained from an organic diisocyanate and a mixture on the basis of diols and macroglycols, in such amounts that the molar ratio of the isocyanate groups to the total sum of the hydroxy groups is within the range of from 1.2 to 2, and preferably is 1.5.

The hydroxy- and/or carboxy-capped fluoropolyethers are used in amounts larger than 1 % by weight, computed relative to the macroglycols, but amounts within the range of from 3 to 20 % by weight, preferably 3 to 15 % by weight, are most commonly used.

The formation of the fluorinated polyisocyanate may be carried out in the presence or in the absence of organic solvents.

In case the reaction is carried out in the presence of solvents, these may be selected from e.g. cellosolve® acetate, acetone, tetrahydrofuran and methyl ethyl ketone.

The reaction temperatures are nearly always lower than 100 °C, and are preferably within the range of from 50 to 90 °C.

The reactions may furthermore be accomplished in the presence of catalysts known in the art, such as the metal-organic compounds, or tertiary amines; examples of such catalysts are: dibutyltin dilaurate, tin octoate, cobalt naphthenate, vanadium acetylacetonate, dimethyltin diethylhexanoate and their mixtures, triethylenediamine, tetramethylguanidine, dimethylcyclohexylamine, and so forth. The preferred catalysts are triethylenediamine and dibutyltin dilaurate. The catalysts are used in catalytic concentrations, and generally at concentrations not higher than 0.1% by weight.

The organic diisocyanates which may be used in the preparation of the aqueous dispersions of the present invention have the general formula $R(NCO)_2$, wherein R represents an alkylene, cycloalkylene, alkylene-cycloalkylene or arylene radical containing from 1 to 20 carbon atoms.

Examples of such diisocyanates are: 2,4-toluenediisocyanate either alone or in admixture with 2,6-toluenediisocyanate isomer, 4,4'-diphenyl-methanediisocyanate, 4,4'-dicyclohexyl-methanediisocyanate, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (or isophorone diisocyanate), 2,4,4-trimethylhexamethylene-diisocyanate, in mixture with 2,4,4-trimethylhexamethylene-diisocyanate isomer, ethylidene-di-isocyanate, butylene-diisocyanate, hexamethylene-diisocyanate, cyclohexylene-1,4-diisocyanate, cyclohexylene-1,2-diisocyanate, xylylene-diisocyanate, dichloro-hexamethylene-diisocyanate, dicyclohexyl-4,4'-diisocyanate, 1-methyl-2,4-diisocyanato-cyclohexane, and 1-methyl-2,6-diisocyanato-cyclohexane. Among these, the aliphatic or cycloaliphatic diisocyanates are preferred when high resistance to U.V. light and to hydrolytic degradation are required.

As ionizable diols, those able to endow the polyurethanic macromolecule with a preferentially anionic charge are preferred, in as much as in such case end products are obtained which are compatible with auxiliary products, pigments, dyes, and aqueous dispersions of a diverse nature (e.g., acrylic, vinylic, butadiene-acrylonitrilic dispersions, etc.), almost totally of an anionic nature.

As ionizable diols, those diols may be used which contain a free carboxyl group, preferably bonded to the same carbon atom which bears the two hydroxyl groups, e.g., dimethylolacetic acid, dimethylolpropionic acid, dimethylolbutyric acid, and so forth.

Furthermore, compounds containing at least two hydroxyl groups and a carboxyl group not bound to the same carbon atom may also be used, such as, e.g., the products of semiesterification of triols with aliphatic dicarboxylic anhydrides.

However, according to the present invention no bar exists against the use of dispersions having a cationic character, by using as ionizable diols the tertiary alkyl-dialkanolamines already known in the art, such as, e.g., methyldiethanolamine, butyldiethanolamine and methyldiisopropanolamine.

The macroglycols which may be used to prepare the aqueous dispersions of the present invention comprises polyols and hydroxy- and/or carboxy-capped fluoropolyethers.

As polyols, those having a molecular weight within the range of from 500 to 5000, preferably of from 800 to 3000, and selected from the class consisting of saturated polyesters, polyethers, polyester-urethanes, polyether-urethanes, polyurethaneamides, may be used.

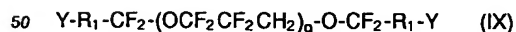
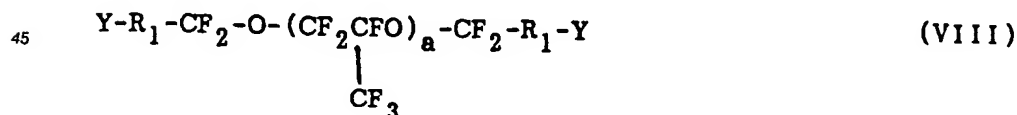
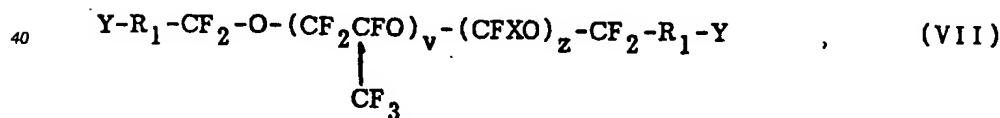
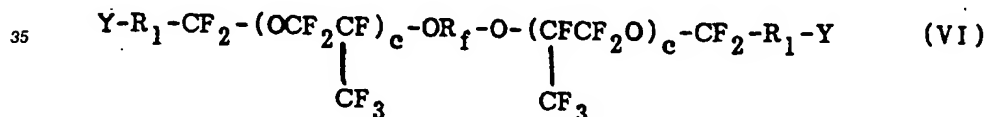
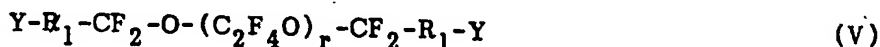
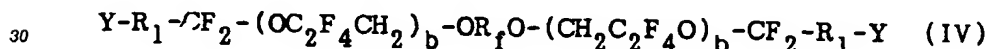
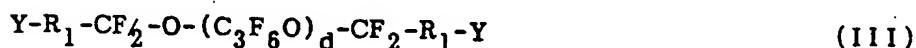
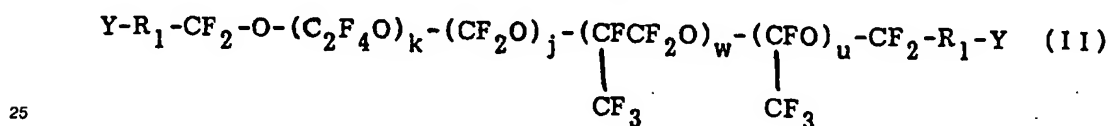
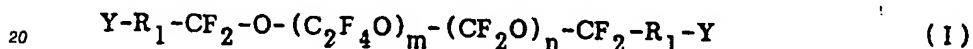
Examples of polyesters are the products of polycondensation of preferably aliphatic dicarboxylic acid anhydrides having from 4 to 9 carbon atoms, such as succinic, adipic, sebacic, azelaic, etc., anhydrides or acids with (C₂-C₈)-aliphatic diols either alone or mixed with one another, such as ethylene glycol, propylene glycol, 1,3- and 1,4-butanediol, 1,6-hexanediol, etc., or the products of polycondensation of ε-caprolactone on diolic "starters".

Examples of polyester-urethanes are the products of polyaddition of the above-mentioned polyesters with organic diisocyanates in molar deficiency.

Examples of polyethers are the various types of polyethylene glycol, polypropylene glycol, and, preferably, the products of polymerization of tetrahydrofuran.

The above-mentioned polyols may be used together with small amounts of low molecular weight polyols, preferably of the trifunctional type, such as trimethylolpropane, glycerol and 1,2,6-hexanetriol.

The hydroxy- and/or carboxy-capped fluoropolyethers have a molecular weight within the range of from 500 to 7 000, preferably of from 1 000 to 2 500, and are selected from the class of those having the formulae:



wherein:

- | | |
|--|--|
| <p>R₁</p> <p>55 m</p> <p>R_f</p> <p>X</p> | <p>is selected from -(CH₂)_x-, -(CH₂O)_yCH₂-, -(CH₂)_xOCH₂-, wherein x and y are integers within the range of from 1 to 4;</p> <p>and n are integers, wherein the m/n ratio is within the range of from 0.2 to 2, preferably within the range of from 0.5 to 1.2;</p> <p>is a perfluoroalkylene radical;</p> <p>if -F or -CF₃;</p> |
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Y represents an -OH and/or a -COOH group; and
 k, j, w, u, d, b, r, c, v, z, a, g are integers which make it possible for the above-mentioned molecular weights to be obtained.

The fluoropolyethers having the above formulae of form (I) to (IX) may be obtained according to processes such as disclosed in US-A-3 242 218; 3 250 808; 3 665 041; 3 810 874 and 4 523 039; and in EP-A-148 482; 151 877; 165 649; and 165 650.

Preferred hydroxy- and/or carboxy-capped fluoropolyethers are α,ω -bis-(hydroxymethyl)-polyoxyperfluoralkylene and α,ω -(polyoxyperfluoroalkene)-dioic acid having an average molecular weight of 2 000, as produced and marketed by Montefluos S.p.A., under the trade marks Fomblin® Z-DOL 2000 and Fomblin® Z-DIAC 2000 respectively.

The salification of the fluorinated polyisocyanate, whether of anionic or cationic type, is preferably carried out in the molten state and may be carried out by simply adding the salifying agent as such, as dissolved in water and/or solvents at temperatures of approximately 90°C; should the molten polyisocyanate have too high a viscosity at such temperatures, diluting it will be suitable, before the salification, with preferably water-miscible solvents having boiling points lower than that of water, so as to make it possible for them to be distilled off.

The amount of solvent normally necessary does not exceed one fifth of the polyisocyanate weight. Examples of suitable solvents are; acetone, methyl-ethylketone, tetrahydrofuran.

For salifying the polyisocyanate of anionic type, salifying agents selected from the class of the inorganic bases, such as sodium or ammonium hydroxide, and the tertiary amines or alkanolamines, such as triethylamine, dimethylethanolamine and methyl-diethanolamine are preferably used.

For salifying the cationic-type polyisocyanates, organic and/or inorganic acids are used, such as hydrochloric, phosphoric, formic, lactic and acetic acid.

After the salification is completed, the fluorinated polyisocyanate may be dispersed in water in all dilutions ratios. Therefore, the salified fluorinated polyisocyanate is dispersed in water so as to have a solids content, variable in dependence of the ionic groups, higher than 20% by weight, and preferably within the range of from 30 to 50% by weight, after the possibly previously-used organic solvent is distilled off.

According to an alternative route, the stable aqueous dispersions of fluorinated polyurethanes containing in their macromolecule hydrophilic ionic groups, either of anionic or cationic nature, may be obtained by means of the following steps:

- (i) preparation of a fluorinated polyisocyanic prepolymer by reacting an organic diisocyanate with a mixture comprising diols containing ionizable groups and macroglycols comprising polyols and at least 1% by weight of one or more hydroxy- and/or carboxy-capped fluoropolyethers;
- (ii) conversion of the fluorinated polyisocyanic prepolymer into an oligo-urethane having unsaturated vinyl end groups, by reacting a compound containing hydroxyls reactive with the isocyanate groups, selected from hydroxy-alkyl-acrylates or -methylacrylates having the formula:



- wherein R_2 is hydrogen or a (C_1 - C_4)-alkyl radical and W is a hydroxyalkyl radical;
- (iii) salification of the so-obtained oligo-urethane to convert the ionizable groups into hydrophilic cations or anions;
- (iv) dispersion of the salified oligo-urethane in water; and
- (v) polymerization of the unsaturated end groups of said oligo-urethane dispersed in water.

The stable aqueous dispersions of fluorinated polyurethanes containing in their macromolecule hydrophilic ionic groups are obtained, according to the present alternative method, according to procedures analogous to those already disclosed.

In particular, the formation of the fluorinated polyisocyanic prepolymer takes place by the reaction between an organic diisocyanate and a mixture constituted by diols and macroglycols in such amounts that the molar ratio between the isocyanate groups and the total number of the hydroxy groups is within the range of from 1.2 to 2, and preferably is 1.5.

The fluorinated polyisocyanic prepolymer is then converted into an oligo-urethane containing ethylenically unsaturated ends groups, by reaction with the hydroxy-alkyl acrylates or methacrylates having

the formula (X) above at temperatures lower than 150°C, and preferably within the range of from 60 to 120°C.

The amount of these acrylates or methacrylates used is determined by the content of free isocyanate groups still present in the polyisocyanic prepolymer; such amounts, as to have NCO-eq/OH-eq ratios within the range of from 0.5 to 1.1, and preferably 1, are the most commonly used.

Preferred hydroxyl-alkyl acrylates or -methacrylates of formula (X) are those wherein R is hydrogen, or a methyl radical, and W is a 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, or 4-hydroxybutyl radical.

The thus-obtained oligo-urethane is salified and dispersed in water according to the procedures disclosed above and is then polymerized by per se known techniques.

The polymerization is carried out by using free-radical generators, e.g., of the type of organic peroxides or hydroperoxides, or of the type of sodium, potassium, ammonium persulphates, etc., either alone or together with such reducing agents as sodium metabisulphite and sodium formaldehyde sulfoxylate.

The polymerization temperature may be within the range from 10 to 100°C, depending on the free radical initiator used.

The aqueous dispersions of the present invention are stable over a long time even in the total absence of surfactants and/or protective colloids. Such a stability is a function of the amount of contained ionic centers, which may be expressed as milliequivalents per 100 g of polymer, considered as the dry substance. Said values may range from 10 to 60 meq/100 g of dry substance, and preferably from 20 to 40 meq/100 g of dry substance.

Because of the ionic character of the polymer, such dispersions are sensitive to electrolytes.

Stabilization thereof may be obtained by means of surfactants and/or protective colloids of non-ionic type, such as ethoxylated derivatives of higher fatty alcohols, or alkylphenols. The use of ionic surfactants must obviously take into account the cationic or anionic nature of the dispersions in question.

The aqueous dispersions of fluorinated polyurethanes of the present invention are preferably used in the preparation or textile articles endowed with contemporaneously high impermeability and breathability.

According to these preparation techniques, either woven or non-woven textile articles, from natural, artificial or synthetic fibers, are treated with such dispersions by coating them on the textile article at dry-deposit levels higher than, or equal to, 20 g/m², and preferably within the range of from 20 to 40 g/m².

Any fibers, or fiber blends, may be used for preparing the textile articles endowed with contemporaneously high impermeability and breathability; examples of suitable natural fibers are wool, silk, cotton, flax, etc.; suitable artificial fibers are cellulosic fibers, and suitable synthetic fibers are acrylic, polyester, polyamidic, and so forth, fibers.

The aqueous dispersions of fluorinated polyurethanes used for the preparation of textile articles endowed with contemporaneously high impermeability and breathability have a solids content within the range of from 20 to 60% by weight, and preferably of from 30 to 50% by weight. These dispersions may be used such, or after the addition to them of suitable thickeners such as, e.g., cellulose ethers, polymeric derivatives based on acrylic acids and/or esters.

The coating process may be performed by the usual techniques, and in particular, by a floating knife or by a knife over roll, plate or blanket.

The degree of penetration of the coated matter into the support fabric may be controlled by means of the viscosity of the paste, or in other ways, according to the prior art, so as to secure the anchoring of the coating, and, at the same time, providing a proper surface covering.

The drying may be performed by any system which makes it possible to remove water at a temperature not higher than 100°C; if desired, adopting expedients that accelerate water release, such as ventilation, pressure reduction, and so forth.

The usual hot-air ovens may be used, with residence times of the order of some minutes when the air temperature is approximately 100°C.

The thus-treated textile article may be subjected to a further thermal treatment, generally within the range of from 100 to 150°C, over short times, to improve the fastness of the polyurethanic deposit.

By using the aqueous dispersion of the present invention, such drawbacks of the prior art as the possible treatments both before and after the application of the dispersion, comprising silicone application, the need for use of impregnating or coupling techniques more complex than the coating of special textile articles, and so forth, may be avoided.

Furthermore, one may contemporaneously achieve high impermeability and breathing characteristics with low levels of polyurethanic deposit, and improved characteristics of fastness of the same deposit to both wet- and dry-washing, and, in general, to wear.

The textile articles, both woven and non-woven, after the treatment with the aqueous dispersions of fluorinated polyurethanes of the present invention, have a permeability to water vapor within the range of

from 900 to 1600 ng/sm² Pa, as measured according to ASTM E 96, and an impermeability to water higher than 24 hours, under a 2-meter water column, as measured according to UNI 5122 Standard.

For the purpose of providing a still better understanding of the present invention, some illustrative but non-limitative examples are given below.

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Example 1

In the preparation of a first fluorinated polyurethane, two operating steps were used for the preparation of the fluorinated polyisocyanate (step a). In the first step, an NCO-capped prepolymer was prepared.

10 For that purpose, 120 g of α, ω -bis (hydroxymethyl)-polyoxyperfluoroalkylene having a molecular weight of 2 000, produced and marketed by Montefluos S.p.A. under the trade mark Fomblin® Z-DOL 2000, 19.7 g of toluenediisocyanate, and 60 g of cellosolve® acetate were charged, with good stirring, to a reactor filled with nitrogen gas, connected with an expansion vessel for nitrogen, kept immersed in a temperature-controlled bath, and equipped with stirrer, thermometer, and reflux condenser.

15 After heating to 40 °C, always with stirring, 0.02 g of triethylenediamine (diazabicyclooctane, DABCO) was added, the temperature was then increased to 80 °C and was maintained at that value for approximately 2 hours, with the exothermicity of the reaction being monitored.

A product was obtained with a content of 70% of dry matter, a content of isocyanate groups of 2.4% by weight, and a molecular weight of approximately 2 400.

20 In the second operative step, the extension of the macromolecular chain and the transfer of the product into the aqueous phase were carried out.

For those purposes, to a reactor analogous to the previous one, 198.89 g of polyoxytetramethylene glycol with an average molecular weight of 1 000 (Terathane® 1000, a product of E.I. du Pont de Nemours), 12.33 g of dimethylolpropionic acid, 22.86 g of the adduct obtained from the previous operative step, and 25 64.83 g of hexamethylenediisocyanate were charged, with the temperature being maintained first at 60 °C for 30 minutes, and then at 75 °C for about 1.5 hours.

A product with 3.1% by weight of free isocyanate groups, referred to the dry substance, was obtained.

Then, 87 g of anhydrous acetone, a solution of 8.18 g of dimethylethanolamine in 165 g of deionized water, and subsequently further 445 g of deionized water were added.

30 Finally, acetone was distilled off. A milky, lowviscosity product was obtained, which contained 31% of dry substance and 4.5% of perfluoro-compound referred to the dry substance.

Example 2

35 The process was carried out as disclosed in Example 1 until a product containing 3.1% by weight, relative to the dry weight, of free isocyanate groups, was obtained. Then, 87 g of anhydrous acetone were added, with the temperature being increased to 60 °C, then 5.28 g of 2-hydroxypropyl acrylate were added, with the atmosphere being changed from nitrogen to dry air. The reaction mixture was maintained at 60 °C until a content of 2.3 % by weight of free isocyanate groups, relative to the dry matter, was attained.

40 With the reaction mixture being sufficiently stirred, a solution of 8.18 g of dimethylethanolamine in 165 g of deionized water, and soon there after 445 g of deionized water, were added. After the mixture was dispersed in water, acetone was distilled off. When distillation was completed, the nitrogen atmosphere was restored, and at a temperature of 50 °C, 1.19 g of tert-butyl-hydroperoxide in aqueous solution at 12 % by weight, diluted with 40 g of H₂, and 0.59 g of sodium formaldehyde sulphonylate dissolved in 40 g of H₂, 45 were added separately within 2 hours.

A milky, low-viscosity product was thus obtained, which contained 31% of dry substance and 4.5% of perfluoro-compound referred to the dry substance.

Example 3

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Step (a) was carried out in one operative step only. To a reactor, analogous to that of Example 1, 227 g of polyoxytetramethylene glycol of the preceding example, 13.7 g of α, ω -(polyoxyperfluoroalkane)-dioic acid having an average molecular weight of 2 000, manufactured and marketed by Montefluos S.p.A. under the trade mark Fomblin® Z-DIAC 2000, 14.47 g of dimethylolpropionic acid, and 77.57 g of hexamethylenediisocyanate, were charged with stirring.

The reaction mixture was heated to 60 °C and maintained at that temperature for 30 minutes; it was then further heated to 75 °C and was maintained at this temperature for 1.5 hours, whereupon a decrease in the content of free isocyanate groups to 3.25% by weight, relative to the dry matter, was detected.

After cooling to 60 °C, 100 g of anhydrous acetone were added, then, after increasing the rate of stirring, an aqueous solution of dimethyl-ethanolamine (10.88 g in 218 g of deionized water) was added within approximately 5 minutes, and soon there after, further 465 g of deionized water were added.

Finally, acetone was distilled off. A milky, low-viscosity product with a content of 30% of dry substance and a level of 4% of perfluoro-compound relative to the dry weight was obtained.

Example 4

The process was carried out as described in Example 3, until a product containing 3.25% by weight, relative to the dry weight, of free isocyanate groups was obtained.

After cooling to 60 °C, 100 g of anhydrous acetone and 628 g of 2-hydroxypropyl acrylate were added, and the atmosphere was changed from nitrogen to dry air. The temperature was maintained at 60 °C until a content of 2.2% by weight of free isocyanate groups, relative to the dry matter, was attained in the reaction mass. Under stirring, to the reaction mixture an aqueous solution of dimethylethanolamine (10.88 g in 218 g of deionized water) was added, over approximately 5 minutes, and soon there after a further 465 g of deionized water were added. Acetone was then distilled off.

When distillation was complete and after the nitrogen atmosphere had been restored the temperature was increased to 50 °C, and during 2 hours 1.95 g of tert-buty-hydroperoxide in an aqueous solution at 12% by weight, diluted in 30 g of water, and 0.97 g of sodium formaldehyde sulphonylate dissolved in 40 g of H₂O were added contemporaneously and separately.

A milky, low-viscosity product was obtained, which contained 30% of dry substance and a level of 4% of perfluoro-compound referred to the dry substance.

Example 5 (comparative example)

An aqueous dispersion of non-fluorinated polyurethanes was prepared for comparative purposes, by operating as in Example 4, but with the difference that α,ω -(polyoxyperfluoroalkane)dioic acid was not used; it was replaced by 6.8 g of polyoxytetramethylene glycol.

A milky, low viscosity product was obtained which contained 30.5 % of dry matter.

Example 6

To 100 parts by weight of a dispersion obtained according to Example 1, 5 parts of an acrylic thickening agent containing 15% by weight of dry matter were added.

To the resulting mixture, an aqueous solution of NH₄OH at 32% by weight of dry matter was added, until a viscosity of 15 000 mPa·s (Brookfield RVT at 20 °C and 20 rpm, spindle 6) was obtained.

The coating paste obtained was applied to a nylon fabric, whose characteristics are reported in Table 1, by a knife over plate. 5 samples with different deposited amounts were prepared.

The coated specimens were then dried in a hot-air oven at 100 °C for 7 minutes, and were then treated at 150 °C for 2 minutes inside the same equipment.

No silicones were applied.

The finished samples were analyzed for the deposited amount (as determined from the difference in weight between the coated fabric and the virgin fabric). These were then subjected to a spray test (UNI 5120) and to tests for impermeability (UNI 5122) and permeability to water vapor (ASTM E 96).

The results are reported in Table 2.

From the values of impermeability, and from the corresponding levels of deposited amounts, a "critical value" of the deposited amount, i.e., the minimum deposited amount for an impermeability of more than 24 hours under a water column of 2 meters, was evaluated.

Example 7

By the same procedure as in Example 6, but starting from the dispersion obtained according to Example 5, 7 samples of coated fabric were prepared and subjected to the same tests, with the results summarized in Table 3.

Example 8

By the same procedure as in Example 6, but starting from the dispersion obtained according to

Example 4, 5 samples of coated fabric were prepared and subjected to the same tests, with the results as summarized in Table 4 being obtained.

Example 9

5

In order to verify their resistance to washing treatments, the samples of Example 6 were treated in a Launder-O-Meter washing machine for 30 minutes at 40 °C, with detergent ECE 77 at 5 parts per thousand and with a bath ratio of 1:20. These were then dried in air and subsequently at 80 °C for 10 minutes, and were finally subjected to the impermeability test. The results are summarized in Table 5.

10

Neither the spray test -- because it is less critical than the impermeability test -- nor the measurement of the permeability to water vapor -- in that it can only improve owing to washing operations -- was carried out.

The results demonstrate the small influence of washing on the applicative characteristics of the textile articles thus treated.

15

Example 10

A further set of samples was prepared with a type of nylon analogous to that used in the above examples, but more permeable to water vapor (permeability of 2 600 instead of 2 175 ng/s m²Pa). These samples were prepared by operating according to the same procedures as in Example 8.

20

The results are reported in Table 6.

Table 1

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Characteristics	Unit of Measure	Values
Chemical composition	-	nylon
Weight per surface unit	g/m ²	65
Warp count	dtex	67
Warp filaments	-	17
Warp insertions	cm ⁻¹	48
Weft count	dtex	78
Weft insertions	cm ⁻¹	33
Weave	-	plain weave
Spray test	-	50
Impermeability (700 mm water column)	mm	0
Permeability to water vapor	ng/sm ² Pa	2,175

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50

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Table 2

5	<u>Tests</u>	Unit of <u>Measure</u>	<u>Samples</u>				
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
	Deposited amount	g/m^2	17	23	35	42	47
10	Spray test	-	90	90	90	90	90
	Impermeability						
	— 700 mm water column	mm	400	700	700	700	700
		min	-	> 10	> 10	> 10	> 10
15	-- 2 m water column	hours	0	> 24	> 24	> 24	> 24
	Permeability to water vapor	$\text{ng/s m}^2 \text{ Pa}$	1096	931	809	792	792
20	Critical deposited amount (c.d.)	g/m^2	20				
	Permeability at c.d.	$\text{ng/s m}^2 \text{ Pa}$	1030				

Table 3

		Samples				
Unit of						
<u>Measure</u>		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
30	Deposited amount	15	23	27	35	43
	SPRAY TEST	-	50	50	50	50
	Impermeability					
35	— 700 mm water column	mm	400	700	700	700
		min	-	2	>10	>10
	— 2 m water column	hours	0	0	0	>24
40	Permeability to water vapor	ng/s m ² Pa	1027	818	905	661
	Critical deposited amount (c. d.)	g/m ²		40		
	Permeability at c. d. .	ng/s m ² Pa		730		

Table 3 (continued)

	Unit of Measure	Samples	
		6	7
Deposited amount	g/m ²	47	54
Spray test	-	50	50
Impermeability			
— 700 mm water column	mm	700	700
	min	> 10	> 10
— 2 m water column	hours	> 24	> 24
Permeability to water vapor	ng/s m ² Pa	705	774
Critical deposited amount (c.d.)	g/m ²		

Table 4

Tests	Unit of Measure	Samples				
		1	2	3	4	5
Deposited amount	g/m ²	17	28	31	38	53
Spray test	-	80	80	80	90	90
Impermeability						
— 700 mm water column	mm	250	700	700	700	700
	min	-	> 10	> 20	> 10	> 10
— 2 m water column	hours	0	> 24	> 24	> 24	> 24
Permeability to water vapor	ng/s m ² Pa	879	914	887	922	757
Critical deposited amount (c.d.)	g/m ²		20			
Permeability at c.d.	ng/s m ² Pa		910			

Table 5

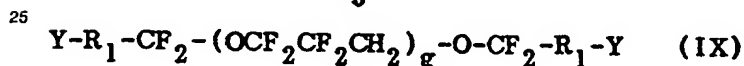
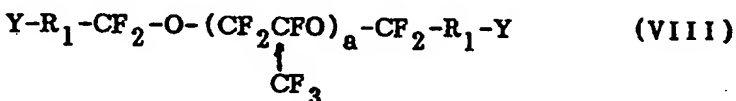
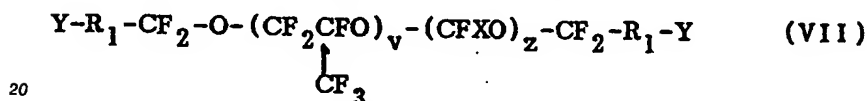
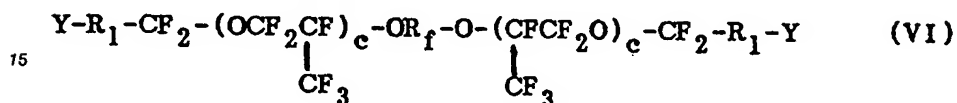
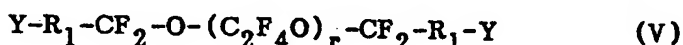
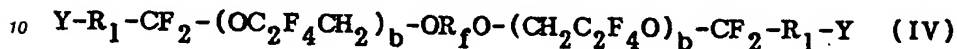
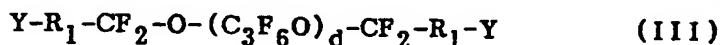
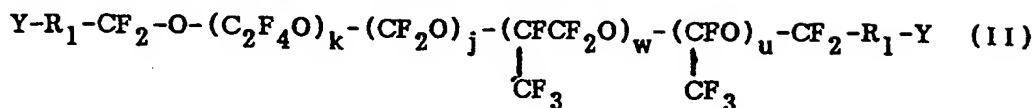
Tests	Units of Measure	Samples				
		1	2	3	4	5
Impermeability after washing						
— 2 m water column	hours	0	< 24	< 24	< 24	< 24

Table 6

Tests	Unit of Measure	Samples				
		1	2	3	4	5
Deposited amount	g/m ²	12	27	36	45	54
Spray test	-	80	80/90	80/90	80/90	80/90
Impermeability						
— 70 mm water column	mm	150	700	700	700	700
	min	-	>10	>10	>10	>10
— 2 m water column	hours	0	>24	>24	>24	>24
Permeability to water vapor	ng/s m ² Pa	1024	1027	1001	948	879
Critical deposited amount (c.d.)	g/m ²	20				
Permeability at c.d.	ng/s m ² Pa	1130				

Claims

1. Stable aqueous dispersions of fluorinated polyurethanes containing in their macromolecules hydrophilic ionic groups, both of anionic and cationic character, obtainable according to the following steps:
 - (a) preparation of a fluorinated polyisocyanate, by reaction between an organic diisocyanate and a mixture comprising diols containing ionizable groups and macroglycols comprising polyols and at least 1 % by weight of one or more hydroxy- and/or carboxy-capped fluoropolyethers;
 - (b) salification of the so-obtained fluorinated polyisocyanate, to convert the ionizable groups into hydrophilic cations or anions; and
 - (c) dispersion and chain extension of the salified fluorinated polyisocyanate in water.
2. Aqueous dispersions according to claim 1, wherein the molar ratio between the isocyanate groups to the sum of the hydroxyl groups is within the range of from 1.2 to 2.
3. Aqueous dispersions according to claim 1, wherein the molar ratio between the isocyanate groups to the sum of the hydroxyl groups is 1.5.
4. Aqueous dispersions according to claim 1 or 2, wherein the macroglycols comprise from 3 to 20% by weight of one or more hydroxy- and/or carboxy-capped fluoropolyethers.
5. Aqueous dispersions according to any one of claims 1 to 4, wherein the hydroxy- and/or carboxy-capped fluoropolyethers have a molecular weight within the range of from 500 to 7000.
6. Aqueous dispersions according to any one of claims 1 to 5, wherein the hydroxy- and/or carboxy-capped fluoropolyethers have a molecular weight within the range of from 1000 to 2500.
7. Aqueous dispersions according to any one of claims 1 to 6, wherein the hydroxy- and/or carboxy-capped fluoropolyethers are selected from those having the formulae:



wherein:

- 30 R_1 is selected from $-(CH_2)_x-$, $-(CH_2O)_yCH_2-$, $-(CH_2)_xOCH_2-$, wherein x and y are integers within the range of from 1 to 4;
- m and n are integers, wherein the m/n ratio is within the range of from 0.2 to 2;
- 35 R_f is a perfluoroalkylene radical;
- X is $-F$ or $-CF_3$;
- Y represents an $-OH$ and/or a $-COOH$ group; and
- $k, j, w, u, d, b, r, c, v, z, a, g$ are integers which make it possible for the above-mentioned molecular weights to be obtained.

40 8. Aqueous dispersions according to claim 7, wherein the ratio m/n ranges from 0.5 to 1.2.

9. Aqueous dispersions according to any one of claims 7 and 8, wherein the hydroxy- and/or carboxy-capped fluoropolyethers are α, ω -bis(hydroxymethyl)-polyoxyperfluoroalkylenes and α, ω -(polyoxyperfluoroalkane)-dioic acids, having an average molecular weight of about 2000.

45 10. Stable aqueous dispersions of fluorinated polyurethanes containing in their macromolecule hydrophilic ionic groups, of either anionic or cationic nature, obtainable by means of the following steps:

- (i) preparation of a fluorinated polyisocyanate prepolymer by reacting an organic diisocyanate with a mixture comprising diols containing ionizable groups and macroglycols comprising polyols and at least 1 % by weight of one or more hydroxy- and/or carboxy-capped fluoropolyethers;
- 50 (ii) conversion of the fluorinated polyisocyanate prepolymer into an oligo-urethane having unsaturated vinyl end groups, by reacting a compound containing hydroxyl groups reactive with the isocyanate groups selected from hydroxyalkyl-acrylates or -methacrylates having the formula:

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wherein R_2 is hydrogen or a (C_1 - C_4)-alkyl radical and W is a hydroxyalkyl radical;

(iii) salification of the oligo-urethane obtained to convert the ionizable groups into hydrophilic cations or anions;

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(iv) dispersion of the salified oligo-urethane in water; and

(v) polymerisation of the unsaturated end groups of said oligo-urethane dispersed in water.

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11. Aqueous dispersions according to claim 10, wherein the hydroxyalkyl-acrylates or -methacrylates are those wherein R_2 is hydrogen or methyl, and W is 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl or 4-hydroxybutyl.

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12. Aqueous dispersions according to claim 10 or 11, wherein the hydroxyalkyl-acrylates or -methacrylates are used in an amount such as to obtain NCO/OH equivalent ratios, in terms of free isocyanate groups present in the polyisocyanate prepolymer, within the range of from 0.5 to 1.1.

13. Aqueous dispersions according to claim 12, wherein the NCO/OH equivalent ratio is equal to 1.

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14. Aqueous dispersions according to any one of claims 1 to 13, having a content of solids higher than 20% by weight.

15. Aqueous dispersions according to any one of claims 1 to 14, having a content of solids within the range of from 30 to 50% by weight.

30

16. Aqueous dispersions according to any one of claims 1 to 15, wherein the fluorinated polyurethanes contain in their macromolecule ionic groups in an amount of from 10 to 60 milliequivalents per 100 g of dry polymer.

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17. Aqueous dispersions according to any one of claims 1 to 16, wherein the fluorinated polyurethanes contain in their macromolecule ionic groups in an amount of from 20 to 40 meq/100 g of dry polymer.

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18. A process for preparing woven and non-woven textile articles, comprising treating said textile articles by means of aqueous dispersions of fluorinated polyurethanes according to any one of claims 1 to 17.

19. A process according to claim 18, wherein the aqueous dispersions of fluorinated polyurethanes are applied by coating them on the textile articles in a dry-deposited amount of at least 20 g/m².

20. A process according to claim 19, wherein the aqueous dispersions of fluorinated polyurethanes are applied by coating them on the textile articles in a dry-deposited amount of 20 to 40 g/m².

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21. A process according to any one of claims 18 to 20, wherein the textile articles are based on natural, artificial or synthetic fibers, such as wool, silk, cotton, flax, cellulosic fibers, acrylic, polyester or polyamide fibers.

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22. Woven and non-woven textile articles treated with stable aqueous dispersions as defined in any one of claims 1 to 17.

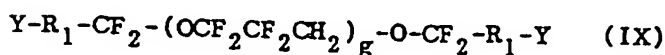
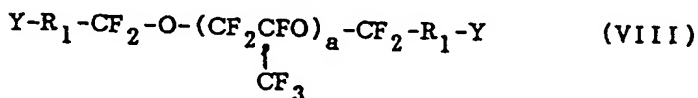
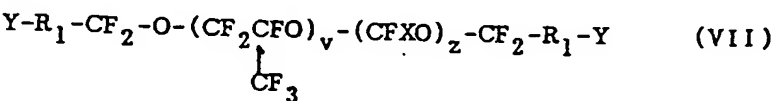
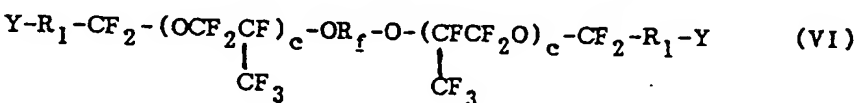
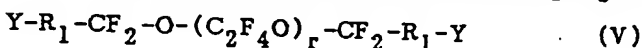
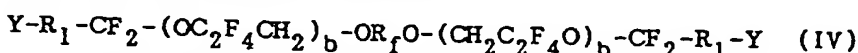
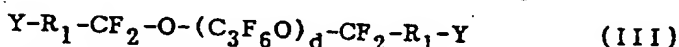
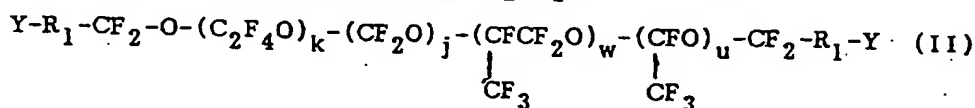
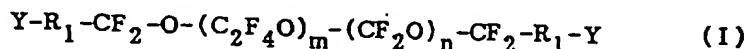
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23. Woven and non-woven textile articles based on natural, artificial or synthetic fibers, such as wool, silk, cotton, flax, cellulosic fibers, acrylic, polyester or polyamide fibers, treated with stable aqueous dispersions as defined in any one of claims 1 to 17.

24. Woven and non-woven textile articles according to claims 22 or 23 endowed with contemporaneously high impermeability and breathability, having a permeability to water vapor within the range of from 900 to 1600 ng/s.m².Pa and impermeability to water of higher than 24 hours under a 2 meter water column.

Revendications

1. Dispersions aqueuses stables de polyuréthanes fluorés dont les macromolécules contiennent des groupes ioniques hydrophiles de caractère soit anionique soit cationique, pouvant être préparées par les étapes suivantes :
 - (a) préparation d'un polyisocyanate fluoré par réaction entre un diisocyanate organique et un mélange comprenant des diols contenant des groupes ionisables et des macroglycols comprenant des polyols et au moins 1% en poids d'un ou de plusieurs fluoropolyéthers à terminaisons hydroxy et/ou carboxy;
 - (b) salification du polyisocyanate fluoré ainsi obtenu, pour convertir les groupes ionisables en anions ou cations hydrophiles; et
 - (c) dispersion et extension de chaîne du polyisocyanate fluoré, salifié dans de l'eau.
2. Dispersions aqueuses suivant la revendication 1, dans lesquelles le rapport molaire des groupes isocyanate à la somme des groupes hydroxy est dans la gamme de 1,2 à 2.
3. Dispersions aqueuses suivant la revendication 1, dans lesquelles le rapport molaire des groupes isocyanate à la somme des groupes hydroxy est de 1,5.
4. Dispersions aqueuses suivant la revendication 1 ou la revendication 2, dans lesquelles les macroglycols comprennent de 3 à 20% en poids d'un ou de plusieurs fluoropolyéthers à terminaisons hydroxy et/ou carboxy.
5. Dispersions aqueuses suivant l'une quelconque des revendications 1 à 4, dans lesquelles les fluoropolyéthers à terminaisons hydroxy et/ou carboxy ont un poids moléculaire dans la gamme de 500 à 7000.
6. Dispersions aqueuses suivant l'une quelconque des revendications 1 à 5, dans lesquelles les fluoropolyéthers à terminaisons hydroxy et/ou carboxy ont un poids moléculaire dans la gamme de 1000 à 2500.
7. Dispersions aqueuses suivant l'une quelconque des revendications 1 à 6, dans lesquelles les fluoropolyéthers à terminaisons hydroxy et/ou carboxy sont choisis parmi ceux qui ont les formules :



dans lesquelles :

- 5 R_1 est choisi parmi $-(CH_2)_x-$, $-(CH_2O)_yCH_2-$, $-(CH_2)_xOCH_2-$, où x et y sont des entiers dans la gamme de 1 à 4;
- m et n sont des entiers, le rapport m/n étant dans la gamme de 0,2 à 2;
- 10 R_1 est un radical perfluoroalkylène;
- X est -F ou $-CF_3$;
- Y représente un groupe -OH et/ou -COOH; et
- k, j, w, u, d, b, r, c, v, z, a, g sont des entiers qui permettent l'obtention des poids moléculaires mentionnés plus haut.

8. Dispersions aqueuses suivant la revendication 7, dans lesquelles le rapport m/n est dans la gamme de 0,5 à 1,2.
- 15 9. Dispersions aqueuses suivant l'une quelconque des revendications 7 et 8, dans lesquelles les fluoropolyéthers à terminaisons hydroxy et/ou carboxy sont des α,ω -bis-(hydroxyméthyl)-polyoxyperfluoroalkylènes et des acides α,ω -(polyoxyperfluoroalcane)-dioïques, ayant un poids moléculaire moyen d'environ 2000.
- 20 10. Dispersions aqueuses stables de polyuréthanes fluorés dont les macromolécules contiennent des groupes ioniques hydrophiles de nature soit anionique soit cationique, pouvant être préparées par les étapes suivantes:
- (i) préparation d'un prépolymère de polyisocyanate fluoré par réaction d'un diisocyanate organique avec un mélange comprenant des diols contenant des groupes ionisables et des macroglycols comprenant des polyols et au moins 1% en poids d'un ou de plusieurs fluoropolyéthers à terminaisons hydroxy et/ou carboxy;
- 25 (ii) conversion du prépolymère de polyisocyanate fluoré en un oligo-uréthane ayant des groupes terminaux vinyliques insaturés, par réaction d'un composé contenant des groupes hydroxy réactifs avec les groupes isocyanate choisi parmi des acrylates ou méthacrylates d'hydroxyalkyle ayant la formule:
- 30



- 35 dans laquelle R_2 est un atome d'hydrogène ou un radical alkyle en C_{1-4} et W est un radical hydroxyalkyle;
- (iii) salification de l'oligo-uréthane obtenu pour convertir les groupes ionisables en anions ou cations hydrophiles;
- 40 (iv) dispersion de l'oligo-uréthane salifié dans de l'eau; et
- (v) polymérisation des groupes terminaux insaturés de cet oligo-uréthane dispersé dans l'eau.

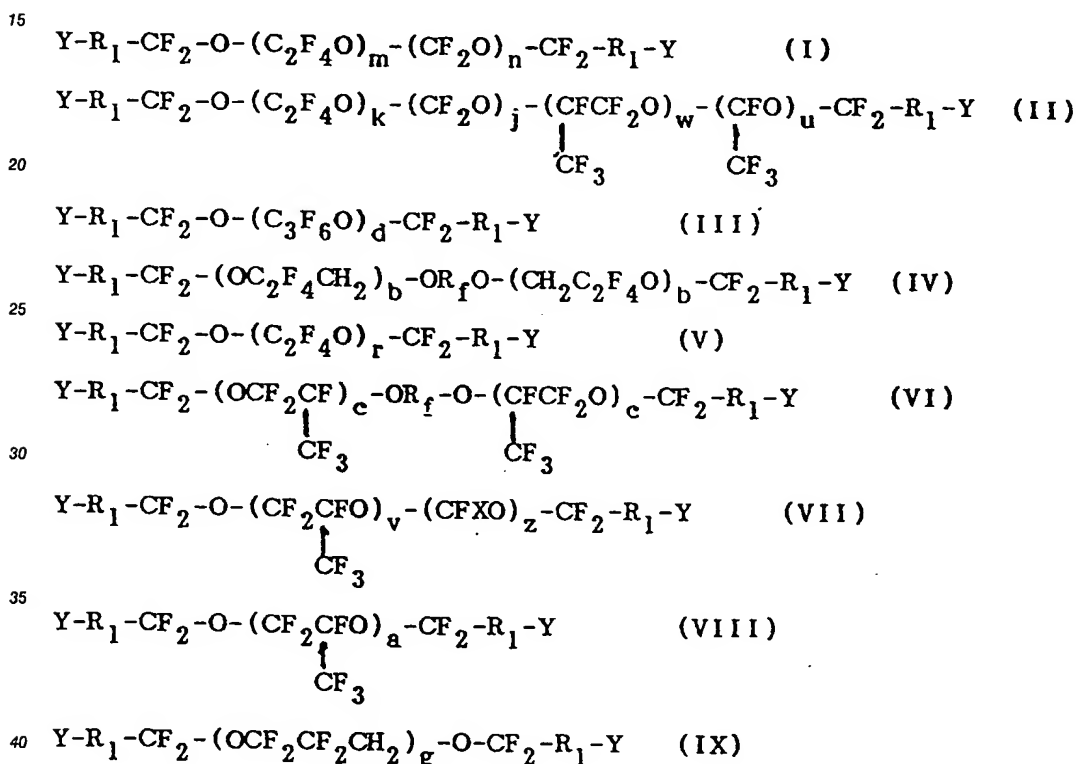
- 45 11. Dispersions aqueuses suivant la revendication 10, dans lesquelles les acrylates ou méthacrylates d'hydroxyalkyle sont ceux dans lequel R_2 est un atome d'hydrogène ou un groupe méthyle, et W est un groupe 2-hydroxyéthyle, 2-hydroxypropyle, 3-hydroxypropyle ou 4-hydroxybutyle.
12. Dispersions aqueuses suivant la revendication 10 ou la revendication 11, dans lesquelles les acrylates ou méthacrylates d'hydroxyalkyle sont utilisés en des quantités telles qu'elles fournissent des rapports NCO/OH équivalents, en termes de groupes isocyanate libres présents dans le prépolymère de polyisocyanate, dans la gamme de 0,5 à 1,1.
- 50 13. Dispersions aqueuses suivant la revendication 12, dans lesquelles le rapport équivalent NCO/OH est égal à 1.
- 55 14. Dispersions aqueuses suivant l'une quelconque des revendications 1 à 13, ayant une teneur en solides supérieure à 20% en poids.

15. Dispersions aqueuses suivant l'une quelconque des revendications 1 à 14, ayant une teneur en solides comprise entre 30 et 50% en poids.
- 5 16. Dispersions aqueuses suivant l'une quelconque des revendications 1 à 15, dans lesquelles les polyuréthanes fluorés contiennent dans leur macromolécule des groupes ioniques en une quantité de 10 à 60 milliéquivalents pour 100 g de polymère sec.
- 10 17. Dispersions aqueuses suivant l'une quelconque des revendications 1 à 16, dans lesquelles les polyuréthanes fluorés contiennent dans leur macromolécule des groupes ioniques en une quantité de 20 à 40 milliéquivalents pour 100 g de polymère sec.
- 15 18. Procédé pour préparer des articles textiles tissés et non-tissés, comprenant le traitement de ces articles textiles avec les dispersions aqueuses de polyuréthanes fluorés suivant l'une quelconque des revendications 1 à 17.
19. Procédé suivant la revendication 18, dans lequel les dispersions aqueuses de polyuréthanes fluorés sont appliquées par enduction sur les articles textiles en une quantité déposée sèche d'au moins 20 g/m².
- 20 20. Procédé suivant la revendication 19, dans lequel les dispersions aqueuses de polyuréthanes fluorés sont appliquées par enduction sur les articles textiles en une quantité déposée sèche de 20 à 40 g/m².
21. Procédé suivant l'une quelconque des revendications 18 à 20, dans lequel les articles textes sont à base de fibres naturelles, artificielles ou synthétiques, comme la laine, la soie, le coton, le lin, des fibres
25 celluloses, des fibres acryliques, polyester ou polyamide.
22. Articles textiles tissés ou non tissés traités avec les dispersions aqueuses stables suivant l'une quelconque des revendications 1 à 17.
- 30 23. Articles textiles tissés ou non tissés à base de fibres naturelles, artificielles ou synthétiques, comme la laine, la soie, le coton, le lin, des fibres celluloses, des fibres acryliques, polyester ou polyamide, traités avec des dispersions aqueuses stables suivant l'une quelconque des revendications 1 à 17.
- 35 24. Articles textiles tissés ou non tissés suivant les revendications 22 ou 23 dotés simultanément de fortes imperméabilité et aptitude à respirer, ayant une perméabilité à la vapeur d'eau de l'ordre de 900 à 1600 ng/s.m².Pa et une imperméabilité à l'eau supérieure à 24 heures sous une colonne de 2 mètres d'eau.

Patentansprüche

- 40 1. Stabile wäßrige Dispersionen von fluorierten Polyurethanen, die hydrophile ionische Gruppen, sowohl anionischer als auch kationischer Natur, in ihren Makromolekülen enthalten, erhältlich durch die folgenden Schritte:
45 (a) Herstellung eines fluorierten Polyisocyanats durch die Reaktion zwischen einem organischen Diisocyanat und einer Mischung, die ionisierbare Gruppen enthaltende Diole und Makroglykole umfaßt, welche Polyole und mindestens 1 Gew.-% eines oder mehrerer mit Hydroxy- und/oder Carboxy-Endgruppen versehenen Fluorpolyether(s) umfassen;
(b) Überführen der so erhaltenen fluorierten Polyisocyanate in Salze, um die ionisierbaren Gruppen in hydrophile Kationen oder Anionen zu überführen; und
50 (c) Dispergieren und Kettenverlängerung der in Salze überführten fluorierten Polyisocyanate in Wasser.
2. Wäßrige Dispersionen nach Anspruch 1, worin das Molverhältnis der Isocyanatgruppen zur Summe der Hydroxylgruppen im Bereich von 1,2 bis 2 liegt.
- 55 3. Wäßrige Dispersionen nach Anspruch 1, worin das Molverhältnis der Isocyanatgruppen zur Summe der Hydroxylgruppen 1,5 beträgt.

4. Wäßrige Dispersionen nach Anspruch 1 oder 2, worin die Makroglykole 3 bis 20 Gew.-% eines oder mehrerer mit Hydroxy- und/oder Carboxy-Endgruppen versehenen Fluorpolyether(s) umfassen.
5. Wäßrige Dispersionen nach irgendeinem der Ansprüche 1 bis 4, worin die mit Hydroxy- und/oder Carboxy-Endgruppen versehenen Fluorpolyether ein Molekulargewicht im Bereich von 500 bis 7000 aufweisen.
6. Wäßrige Dispersionen nach irgendeinem der Ansprüche 1 bis 5, worin die mit Hydroxy- und/oder Carboxy-Endgruppen versehenen Fluorpolyether ein Molekulargewicht im Bereich von 1000 bis 2500 aufweisen.
7. Wäßrige Dispersionen nach irgendeinem der Ansprüche 1 bis 6, worin die mit Hydroxy- und/oder Carboxy-Endgruppen versehenen Fluorpolyether ausgewählt sind aus solchen der Formeln:



worin:

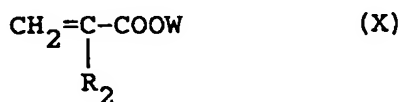
- R_1 aus $-(CH_2)_x-$, $-(CH_2O)_yCH_2-$ und $-(CH_2)_xOCH_2-$ ausgewählt ist, worin x und y ganze Zahlen im Bereich von 1 bis 4 sind;
- m und n ganze Zahlen sind, wobei das Verhältnis m/n im Bereich von 0,2 bis 2 liegt;
- R_f ein Perfluoralkylenrest ist;
- X -F oder $-CF_3$ darstellt;
- Y eine -OH- und/oder eine -COOH-Gruppe repräsentiert; und
- $k, j, w, u, d, b, r, c, v, z, a, g$ ganze Zahlen sind, derart, daß die oben genannten Molekulargewichte erhalten werden können.

8. Wäßrige Dispersionen nach Anspruch 7, worin das Verhältnis m/n im Bereich von 0,5 bis 1,2 liegt.
9. Wäßrige Dispersionen nach irgendeinem der Ansprüche 7 und 8, worin die mit Hydroxy- und/oder Carboxy-Endgruppen versehenen Fluorpolyether α, ω -Bis(hydroxymethyl)polyoxyperfluoralkylene und α, ω -(Polyoxyperfluoralkan)dicarbonsäuren mit einem durchschnittlichen Molekulargewicht von etwa

2000 sind.

10. Stabile wäßrige Dispersionen von fluorierten Polyurethanen, die hydrophile ionische Gruppen, entweder anionischer oder kationischer Natur, in ihrem Makromolekül enthalten, erhältlich durch die folgenden Schritte:

- 5 (i) Herstellung eines fluorierten Polyisocyanat-Prepolymers durch Umsetzung eines organischen Diisocyanats mit einer Mischung, die ionisierbare Gruppen enthaltende Diole und Makroglykole umfaßt, welche Polyole und mindestens 1 Gew.-% eines oder mehrerer mit Hydroxy- und/oder Carboxy-Endgruppen versehenen Fluorpolyether(s) umfassen;
- 10 (ii) Umwandlung des fluorierten Polyisocyanat-Prepolymers in ein Oligourethan mit ungesättigten Vinylendgruppen durch die Umsetzung mit einer Verbindung, welche Hydroxylgruppen enthält, die mit den Isocyanatgruppen reagieren können, ausgewählt aus Hydroxyalkyl-acrylaten oder -methacrylaten der Formel



- 20 worin R_2 Wasserstoff oder ein (C_1-C_4) -Alkylrest ist und W einen Hydroxyalkylrest darstellt;
- (iii) Überführen des erhaltenen Oligourethans in ein Salz, um die ionisierbaren Gruppen in hydrophile Kationen oder Anionen zu überführen;
- (iv) Dispergieren des in ein Salz überführten Oligourethans in Wasser; und
- 25 (v) Polymerisieren der ungesättigten Endgruppen des in Wasser dispergierten Oligourethans.

11. Wäßrige Dispersionen nach Anspruch 10, worin die Hydroxyalkylacrylate oder -methacrylate solche sind, in denen R_2 Wasserstoff oder Methyl ist und W 2-Hydroxyethyl, 2-Hydroxypropyl, 3-Hydroxypropyl oder 4-Hydroxybutyl bedeutet.
- 30 12. Wäßrige Dispersionen nach Anspruch 10 oder 11, worin die Hydroxyalkylacrylate oder -methacrylate in einer solchen Menge eingesetzt werden, um NCO/OH-Äquivalentverhältnisse, bezogen auf freie Isocyanatgruppen, die im Polyisocyanat-Prepolymer anwesend sind, im Bereich von 0,5 bis 1,1 zu erhalten.
- 35 13. Wäßrige Dispersionen nach Anspruch 12, worin das NCO/OH-Äquivalentverhältnis gleich 1 ist.
14. Wäßrige Dispersionen nach irgendeinem der Ansprüche 1 bis 13 mit einem Feststoffgehalt größer als 20 Gew.-%.
- 40 15. Wäßrige Dispersionen nach irgendeinem der Ansprüche 1 bis 14 mit einem Feststoffgehalt im Bereich von 30 bis 50 Gew.-%.
16. Wäßrige Dispersionen nach irgendeinem der Ansprüche 1 bis 15, worin die fluorierten Polyurethane ionische Gruppen in einer Menge von 10 bis 60 Milliäquivalenten pro 100 g trockenem Polymer in ihrem Makromolekül enthalten.
- 45 17. Wäßrige Dispersionen nach irgendeinem der Ansprüche 1 bis 16, worin die fluorierten Polyurethane ionische Gruppen in einer Menge von 20 bis 40 Milliäquivalenten/100 g trockenem Polymer in ihrem Makromolekül enthalten.
- 50 18. Verfahren zur Herstellung gewobener und nicht-gewobener Textilartikel, umfassend die Behandlung der Textilartikel mit wäßrigen Dispersionen fluorierter Polyurethane nach irgendeinem der Ansprüche 1 bis 17.
- 55 19. Verfahren nach Anspruch 18, worin die wäßrigen Dispersionen fluorierter Polyurethane aufgebracht werden, indem die Textilartikel damit in einer Menge von mindestens 20 g/m² Trockengewicht beschichtet werden.

20. Verfahren nach Anspruch 19, worin die wäßrigen Dispersionen fluorierter Polyurethane aufgebracht werden, indem die Textilartikel damit in einer Menge von 20 bis 40 g/m² Trockengewicht beschichtet werden.
- 5 21. Verfahren nach irgendeinem der Ansprüche 18 bis 20, worin die Textilartikel auf natürlichen, künstlichen oder synthetischen Fasern basieren, z.B. Wolle, Seide, Baumwolle, Flachs, Cellulosefasern, Acryl-, Polyester- oder Polyamidfasern.
- 10 22. Gewobene und nicht-gewobene Textilartikel, die mit stabilen wäßrigen Dispersionen nach irgendeinem der Ansprüche 1 bis 17 behandelt worden sind.
- 15 23. Gewobene und nicht-gewobene Textilartikel, basierend auf natürlichen, künstlichen oder synthetischen Fasern, z.B. Wolle, Seide, Baumwolle, Flachs, Cellulosefasern, Acryl-, Polyester- oder Polyamidfasern, die mit stabilen wäßrigen Dispersionen nach irgendeinem der Ansprüche 1 bis 17 behandelt worden sind.
- 20 24. Gewobene und nicht-gewobene Textilartikel nach den Ansprüchen 22 oder 23, die gleichzeitig hohe Undurchlässigkeit und Atmungsfähigkeit aufweisen, mit einer Wasserdampf-Durchlässigkeit im Bereich von 900 bis 1600 ng/ s·m²·Pa und einer Wasser-Undurchlässigkeit von mehr als 24 Stunden unter einer Wassersäule von 2 m.

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